



TITLE:

# <International Research Center for Elements Science>Advanced Solid State Chemistry

AUTHOR(S):

---

CITATION:

<International Research Center for Elements Science>Advanced Solid State Chemistry. ICR Annual Report 2011, 18: 54-55

ISSUE DATE:

2011

URL:

<http://hdl.handle.net/2433/154948>

RIGHT:

# International Research Center for Elements Science – Advanced Solid State Chemistry –

<http://www.scl.kyoto-u.ac.jp/~shimakgr/indexE.html>



Prof  
SHIMAKAWA, Yuichi  
(D Sc)



Assist Prof  
KAN, Daisuke  
(D Sc)



Assist Prof  
SAITO, Takashi  
(D Sc)



Program-Specific Assist Prof  
ICHIKAWA, Noriya  
(D Eng)



PD  
CHEN, Wei-tin  
(Ph D)



PD  
ZHANG, Shoubao  
(Ph D)

## Students

TOHYAMA, Takenori (D2)  
MATSUMOTO, Kazuya (D2)  
AOYAMA, Chihiro (M2)  
SEKI, Hayato (M2)

HIRAI, Kei (M2)  
SHIMIZU, Takuya (M1)  
NISHI, Hitomi (M1)  
YAMADA, Marina (M1)

## Visitor

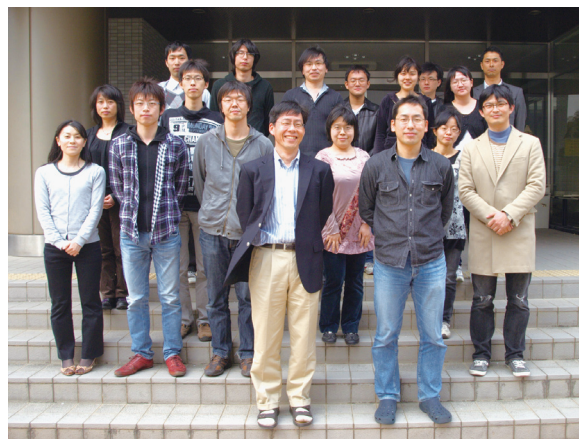
Prof Kennedy, Brendan School of Chemistry The University of Sydney, Australia, 10–22 July

## Scope of Research

Transition metal oxides display a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides have been used in current electronic devices. Our research mainly focuses on perovskite-structured transition metal oxides with novel functional properties due to complex couplings between their lattices, charges and spins. With advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth, we are currently exploring such functional oxides.

### KEYWORDS

Solid State Chemistry  
Functional Transition Metal Oxides  
Epitaxial Thin Film Growth  
High Pressure Synthesis  
Perovskite Structured Oxides



## Selected Publications

Matsumoto, K.; Haruta, M.; Kawai, M.; Sakaiguchi, A.; Ichikawa, N.; Kurata, H.; Shimakawa, Y., Selective Reduction of Layers at Low Temperature in Artificial Superlattice Thin Films, *Sci. Reports*, **1**, 27 (2011).  
Azuma, M.; Chen, W. T.; Seki, H.; Czapski, M.; Olga, S.; Oka, K.; Mizumaki, M.; Watanuki, T.; Ishimatsu, N.; Kawamura, N.; Ishiwata, S.; Tucker, M. G.; Shimakawa, Y.; Attfield, J. P., Colossal Negative Thermal Expansion in BiNiO<sub>3</sub> Induced by Intermetallic Charge Transfer, *Nat. Comm.*, **2**, 347 (2011).  
Inoue, S.; Kawai, M.; Ichikawa, N.; Kageyama, H.; Paulus, W.; Shimakawa, Y., Anisotropic Oxygen Diffusion at Low Temperature in Perovskite-Structure Iron Oxides, *Nat. Chem.*, **2**, 213-217 (2010).  
Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y., Temperature-induced A-B Intersite Charge Transfer in an A-site-ordered LaCu<sub>3</sub>Fe<sub>4</sub>O<sub>12</sub> Perovskite, *Nature*, **458**, 60-63 (2009).  
Kan, D.; Terashima, T.; Kannda, R.; Masuno, A.; Tanaka, K.; Chu, S.; Kan, H.; Ishizumi, A.; Kanemitsu, Y.; Shimakawa, Y.; Takano, M., Blue-light Emission at Room Temperature from Ar<sup>+</sup>-irradiated SrTiO<sub>3</sub>, *Nat. Mater.*, **4**, 816-819 (2005).

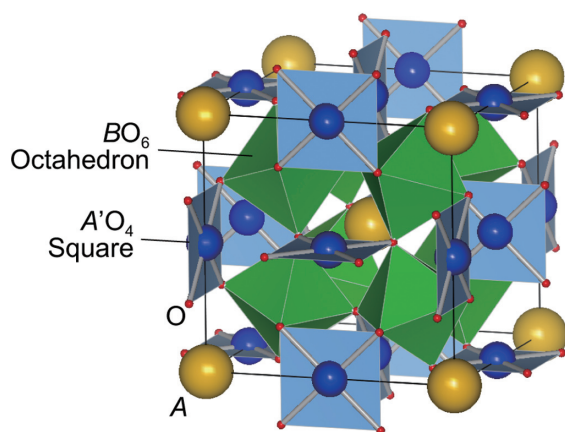
## Material Design and High-pressure Synthesis of Novel A-site-ordered Perovskites

A-site-ordered perovskite oxides with chemical formula  $AA'_3B_4O_{12}$  have a rich variety of physical and chemical properties, such as intersite charge transfer. To further explore novel compounds with this A-site-ordered structure, we evaluated structural stability by calculating the global instability index (GII) with the SPuDS program and designed new compounds based on the calculation results. We especially focus on the compound with  $Mn^{3+}$  in the square-planar  $A'$  site,  $A^{3+}Mn^{3+}_3Al^{3+}_4O_{12}$  because the square-planar coordination of the  $Mn^{3+}$  ion is very rare in oxide materials, and it is expected that such unique coordination would have unusual electronic structure and results in interesting magnetic properties. Also selecting the non magnetic  $Al^{3+}$  ion in B-site makes it easier to investigate how the square-planarly coordinated  $Mn^{3+}$  ion magnetically behaves.

From the structural stability of hypothetical  $AMn_3Al_4O_{12}$  ( $A$  = lanthanoid ions or Y ions), we find that the ionic radius in the A-site ion  $r_A$  increases, GII first decreases and reaches a minimum for Dy of which  $r_A$  is 1.08 Å. With further increasing  $r_A$ , the GII increases. This suggests that with the  $A^{3+}$  ions having  $r_A$  near 1.08 Å, the  $AMn_3Al_4O_{12}$  structure become most stable. Thus we selected Y, Yb, and Dy for the A-site elements.

With high-pressure synthesis technique we have succeeded in synthesizing those designed compounds with a cubic  $Im\bar{3}m$   $AA'_3B_4O_{12}$  perovskite structure.

Structural parameters obtained from the structure refinement well agreed with the “predicted” values. Magnetic property measurements revealed that the  $Mn^{3+}$  ions at the square-planar A-site provides  $S = 2$  spins, which are antiferromagnetically ordered at temperatures ranging from 29 to 40 K due to the direct exchange interaction. It is also found that the moment of  $Yb^{3+}$  and  $Dy^{3+}$  ion showed paramagnetic behaviors even below the antiferromagnetic transition temperatures.

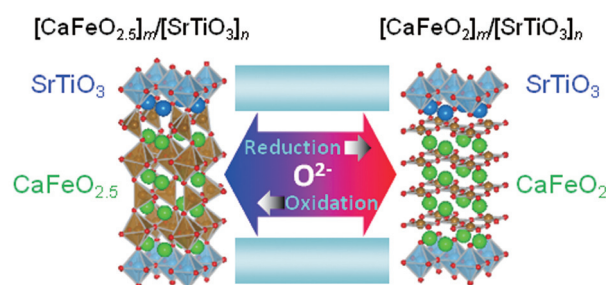


**Figure 1.** Crystal structure of A-site-ordered provskite  $AA'_3B_4O_{12}$ .

## Selective Reduction of Layers at Low Temperature in Artificial Superlattice Thin Films

Oxygen-deficient perovskites  $AFeO_{3-\delta}$  ( $A$  = Sr or Ca and  $\delta = 0\sim 1.0$ ) attract much attention because they show wide varieties in crystal structures and physical properties as a function of oxygen content, and thus they have been studied extensively for more than 40 years. For example,  $SrFeO_3$  ( $\delta = 0$ ) is a simple perovskite, contains iron ions with unusually high valence state ( $Fe^{4+}$ ), which is stabilized by a strong oxidizing atmosphere, and exhibits metallic conductivity.  $SrFeO_{2.5}$  ( $\delta = 0.5$ ), on the other hand, is synthesized at an ambient condition, and its brownmillerite structure consists of alternate layers of  $Fe^{3+}$  octahedra and tetrahedra, and is an antiferromagnetic insulator. It has been demonstrated that low-temperature topochemical reduction can make the brownmillerite  $SrFeO_{2.5}$  to an infinite-layer structure  $SrFeO_2$  ( $\delta = 1.0$ ). Such a wide range of oxygen nonstoichiometry could also be exploited in applications for electrochemical energy generation and storage devices.

Recently we found the selective topochemical reduction occurs when artificial superlattices with transition-metal oxides are treated at a temperature below 300°C with  $CaH_2$ .  $[CaFeO_{2.5}]_m/[SrTiO_3]_n$  infinite-layer/perovskite artificial superlattice thin films were obtained by low-temperature reduction of  $[CaFeO_{2.5}]_m/[SrTiO_3]_n$  brownmillerite/perovskite artificial superlattice thin films. By the reduction only the  $CaFeO_{2.5}$  layers in the artificial superlattices were reduced to the  $CaFeO_2$  infinite layers whereas the  $SrTiO_3$  layers were unchanged. The observed low-temperature reduction behaviors strongly suggest that the oxygen ion diffusion in the artificial superlattices is confined within the two-dimensional brownmillerite layers and the stable  $SrTiO_3$  layers can act as barriers for the oxygen diffusion. The reduced artificial superlattice could be reoxidized, and thus, the selective reduction and oxidation of the constituent layers in the perovskite-structure framework occur reversibly.



**Figure 2.** Reversible changes from  $[CaFeO_{2.5}]_m/[SrTiO_3]_n$  to  $[CaFeO_2]_m/[SrTiO_3]_n$  superlattice. The oxygen ion diffusion is confined within the two-dimensional brownmillerite layers.